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A novel differential LAPS with PVC and HfO_2 sensing membranes for pH sensors

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1. Introduction

The light-addressable potentiometric sensor (LAPS) is a semiconductor-based chemical or biomedical sensor with an electrolyte-insulator-semiconductor (EIS) structure proposed by Hafeman in 1988. [1] The generated photocurrent corresponding to surface potential is measured by illuminating parts of the semiconductor substrate with infrared light. The amplitude of generated photocurrent depends on the local surface potential between sensing surface and electrolyte. Due to the simple fabricated-process, easy encapsulation and light addressability for multi-ions sensing, LAPS technology were extensively studied as a sensor platform to replace other semiconductor-based chemical sensors. In recent year, the differential mode measurement system of LAPS was introduced for compensating the effect caused by some disturbing factors such as temperature variation, pH variation of solution, and drift of the output signal with time, and so on for precise measurement. [2] However, the difference between two signals of the proposed different mode measurement system by illuminating different position or electrode area is tiny and difficult to generate the differential photo current.

In this article, by using two kinds of sensing membrane with different pH sensitivity to enhance the differential signal was proposed. The differential photocurrent was extracted from a simple differential OP-amplifier circuit by connecting two separated Al electrodes corresponding to each sensing membranes. A PVC membrane fabricated by commercially available chemicals deposited on HfO_2 membrane was chosen as reference membrane to compare with bare HfO_2 membrane. Comparing the effort of proposed differential system in this work, the sensitivity of LAPS structures with each sensing membrane and LAPS structures with both sensing membranes were all measured.

2. Experimental

To investigate the hydrogen ion sensing properties, the LAPS structure were fabricated. P-type silicon wafer was used as starting substrate. Then a 50 nm thick silicon oxide was thermally grown in dry oxygen after initial cleaning (RCA). For sensing membrane fabrication, a 40 nm thick HfO_2 layer was deposited by reactive r.f. sputtering method. Then the thermal treatment by rapid thermal annealing (RTA) method was performed on HfO_2 LAPS devices in nitrogen gas at 700℃ for one minute due to the process optimization. [3] After removing negative oxide, a 300 nm Al film was evaporated on backside of the silicon wafer to form the ohmic contact. Finally, a hand made epoxy with red glue was used to define the sensing area. To study the influence of the compositions of PVC membrane on pH sensitivity, weight percentages on DNP in respect to total weight on DNP and PVC (DNP + PVC) were adjusted and tested on LAPS system. The volume of PVC cocktail with various weight percentages on DNP were deposited on the HfO_2 surface are varied due to the sensing area different. The optimized DNP weight is 60% DNP of DNP + PVC.

To optimize the stability and adhesion between PVC membrane and HfO_2 layer. The surface was firstly cleaned by ethanol washing and DI water flushing. Afterwards, the surfaces were silyated with silylating solution , which is HMDS diluted in toluene with the volume ration 1:3.

After silylation process, PVC membrane were deposited using the various DNP PVC cocktail. Finally, the sensor was treated at room temperature for at least 12 hours. The simple PVC membrane process flow is shown in Fig 1.

3. Parameters extraction

The basic concept of differential measurement system with LAPS structure is shown in Fig. 2. The electron-hole pairs were generated by an IR-LED illumination on backside surface of silicon wafer. Due to the potential of the sensing surface respect to reference electrode, the photocurrent was produced depending on the width of the depletion layer. The sensitivity is depended on the surface interaction with the analyte and form an additional potential, which varies the width of the depletion layer. The variation of the photo current from two electrodes were different and were corresponded to the different sensing membrane.

A differential OP-amplifier was used to amplify the differential signal from these two electrodes. Due to both photocurrents were generated by one IR-LED, the phase shift could be neglected. The flat band voltages corresponding to each membrane could be measured separately.

4. Results and discussion

For LAPS structures with each sensing membrane, the pH-sensitivity of HfO_2 LAPS is 59 mV/pH as shown in Fig 3(a) and the pH-sensitivity of 60% DNP PVC LAPS is 24 mV/pH as shown in Fig 3(b). The ideal differential pH-sensitivity between these two LAPS structures should be 35 mV/pH but the real differential pH-sensitivity extracted from differential circuit is 30 mV/pH as shown in Fig 3(c). The lower pH sensitivity of the differential circuit was obtained due to the discrepancy of sensing area or superimpose of each photo current. To confirm the distinction of the signal extracted form these two electrodes of LAPS structure, the ground contact or floating contact testing were performed. In ground contact testing, the signal is extracted form one electrode and the other electrode is connected to ground at the same time. The results of shifted I-V curves and extracted flat-band voltages were shown in Fig 4. In floating contact testing, the signal is extracted form one electrode and the other electrode is connected to ground at the same time. The results of shifted I-V curves and

extracted flat-band voltages were shown in Fig 5. The pH-sensitivity of PVC membrane in ground contact testing is 33.4 mV/pH and the pH-sensitivity of PVC membrane in floating contact testing is 44.5 mV/pH. It is indicated that the photocurrent could be easily separated in ground contact between both electrodes but the photocurrent could be easily affected by another electrode in floating contact.

5. Conclusions

In this article, the differential measurement system of LAPS using two different pH-sensitive membranes was proposed. By using 60% DNP/DNP+PVC membrane deposited on HfO_2, the differential pH-sensitivity could be measured and attain to 30 mV/pH. To confirm the distinction of the signal extracted form these two electrodes on single LAPS structure, the ground contact or floating contact testing were performed. And the results show that the ground contact is more suitable for differential signal extraction.

Reference

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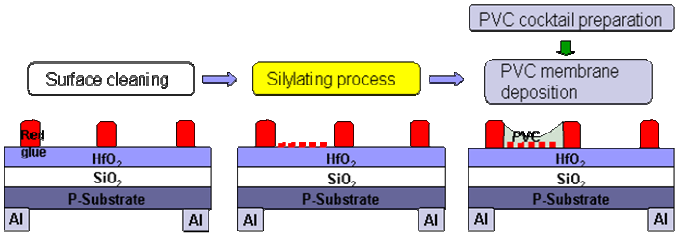


Fig. 1 The simple process flow of LAPS structure fabrication with the PVC membrane.

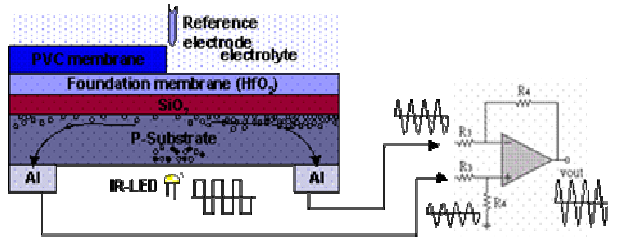
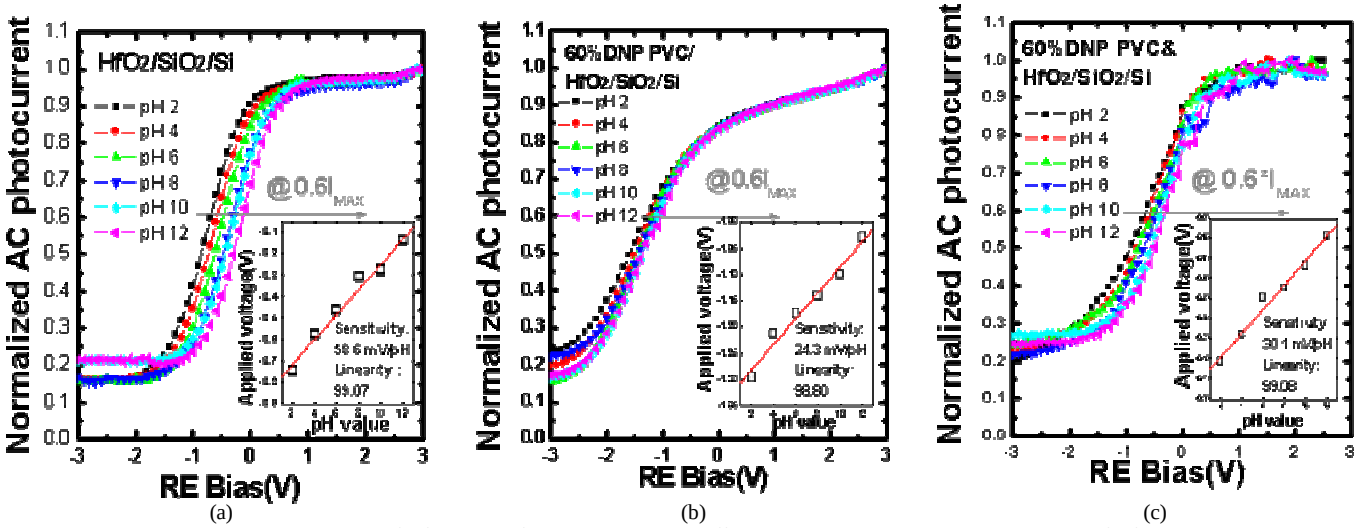
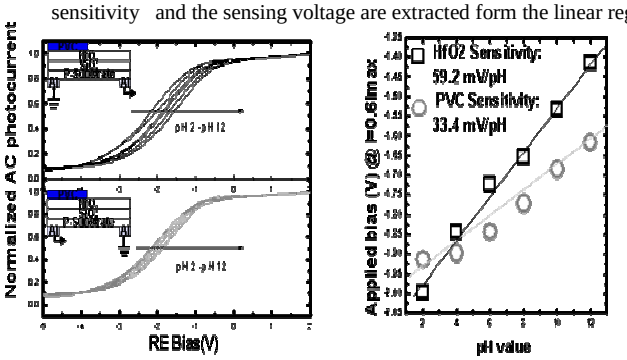


Fig 2 The concept of LAPS differential measuremet system and principle



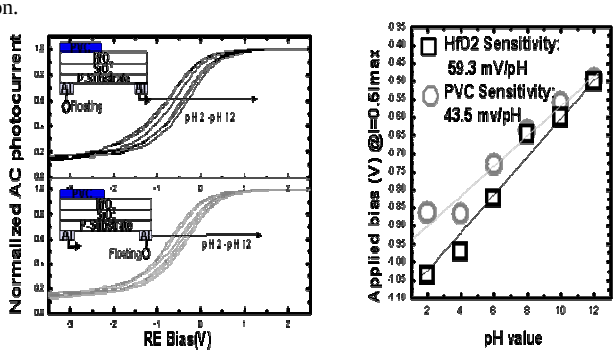
(a) (b) (c)

Fig 3 (a) The measured I-V curves of HfO2 LAPS from pH 2 to pH 12 buffer solutions. (b) The measured I0V curves of HfO2 LAPS with PVC (DNP 60% of DNP+PVC) membrane from pH 2 to pH 12 buffer solutions. (c) The measured differential I-V curves between HfO2 LAPS and HfO2 LAPS with PVC (DNP 60% of DNP+PVC) membrane from pH 2 to pH 12 buffer solutions. The inset figures in each figure are shown the fitting slope of sensitivity and the sensing voltage are extracted form the linear region.



(a) (b)

Fig 4 (a) The measured I-V curves of ground contact testing on HfO2 LAPS and HfO2 LAPS with PVC (DNP 60% of DNP+PVC) membrane from pH 2 to pH 12 buffer solutions. (b) The fitting slope of sensitivity and extracted sensing voltage in linear region of HfO2 LAPS and HfO2 LAPS with PVC (DNP 60% of DNP+PVC) membrane.



(a) (b)

Fig 5 (a) The measured I-V curves of floating contact testing on HfO2 LAPS and HfO2 LAPS with PVC (DNP 60% of DNP+PVC) membrane from pH 2 to pH 12 buffer solutions. (b) The fitting slope of sensitivity and extracted sensing voltage in linear region of HfO2 LAPS and HfO2 LAPS with PVC (DNP 60% of DNP+PVC) membrane.